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**High-Altitude Aircraft and Balloon-Borne Observations  
of OH, HO<sub>2</sub>, ClO, BrO, NO<sub>2</sub>, ClONO<sub>2</sub>, ClOOCl, H<sub>2</sub>O, and O<sub>3</sub>  
in Earth's Stratosphere**

Progress Report  
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Research executed over calendar year 1995 focused on three primary objectives. The first is the dissection of free radical catalytic cycles. The objective is to determine both the mechanisms for ozone loss in the lower stratosphere, by establishing the hierarchy of rate limiting steps in the nitrogen, halogen, and hydrogen cycles, and to determine the response of the stratosphere to changing levels of  $\text{NO}_x$ , aerosols, etc., by directly observing the partial derivatives of the constituent concentrations. Observations are made from the NASA ER-2 aircraft. The second is to incorporate fast-response water vapor measurements into the ER-2 payload, to obtain high spatial resolution data on water vapor. This is a particularly powerful technique for diagnosing dynamical behavior of the stratosphere when combined with the rapid time-response  $\text{CO}_2$  observations available on the ER-2. The third objective is the development of a new instrument designed for the ER-2 superpod, which will observe  $\text{ClONO}_2$  *in situ* for the first time, and also will observe  $\text{ClO}$ ,  $\text{BrO}$ , and  $\text{NO}_2$  simultaneously. We present the progress made in each category.

With respect to the observation of free radicals from the ER-2, observations obtained during the ASHOE/MAESA mission extended  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{ClO}$  and  $\text{BrO}$  measurements from the Arctic to the Antarctic. Simultaneous, *in situ* measurements of the concentrations of  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{ClO}$ ,  $\text{BrO}$ ,  $\text{NO}$ , and  $\text{NO}_2$  demonstrate the predominance of odd-hydrogen and halogen free-radical catalysis in determining the rate of removal of ozone in the lower stratosphere. A single catalytic cycle, in which the rate-limiting step is the reaction of  $\text{HO}_2$  with ozone, accounted for nearly one-half of the total  $\text{O}_3$  removal in this region of the atmosphere. Halogen-radical chemistry was responsible for approximately one-third of the photochemical removal of  $\text{O}_3$ ; reactions involving  $\text{BrO}$  account for one-half of this loss. Catalytic destruction by  $\text{NO}_2$ , which for two decades was considered to be the predominant loss process, accounted for less than 20% of the  $\text{O}_3$  removal. The measurements demonstrate quantitatively the coupling that exists between the radical families. The concentrations of  $\text{HO}_2$  and  $\text{ClO}$  are inversely correlated with those of  $\text{NO}$  and  $\text{NO}_2$ . The direct determination of the relative importance of the catalytic loss processes, combined with a demonstration of the reactions linking the hydrogen,

halogen, and nitrogen radical concentrations, shows that, in the air sampled, the rate of  $O_3$  removal was inversely correlated with total  $NO_x$  loading.

These observations, extended to latitudes from  $60^\circ S$  to  $60^\circ N$  under “normal” aerosol loading following the elimination of Mt. Pinatubo aerosols, have significantly changed our understanding of the impact of stratospheric aircraft  $NO_x$  emissions on the lower stratosphere. Rather than enhancing ozone loss, the release of  $NO_x$  may well decrease the ozone loss rate in the lower stratosphere. The higher altitudes, above the ER-2 ceiling, remain a major issue. These observations have, on the other hand, heightened concern over the release of aerosols into a halogen-rich stratosphere, providing an explanation for the rapid decrease in ozone over mid latitudes following the eruption of Mt. Pinatubo in 1991.

This research has focused also on the bromine catalytic destruction of ozone. Observations of the BrO radical in the lower stratosphere, obtained simultaneously with measurements of short-lived hydrogen, nitrogen and chlorine radicals and long-lived radical precursors, demonstrate that reactions involving bromine account for more than half of the catalytic destruction of ozone by halogens at  $\sim 20$  km. In the air masses sampled using the ER-2 aircraft, bromine is 60–80 times more efficient at ozone removal than chlorine on a per-atom basis. An inferred value for total stratospheric bromine agrees within error with measurements of the bromine source species, the organic bromine compounds that enter the stratosphere from the troposphere.

In the course of the ASHOE/MAESA mission, the ER-2 successfully intercepted the exhaust plume of the Concorde supersonic aircraft as it approached Christchurch, New Zealand. The ER-2 was also vectored properly so as to observe its own effluent in the stratosphere. Thus, concentrations of OH and  $HO_2$  have been measured in the exhaust of an Air France Concorde and a NASA ER-2 in the lower stratosphere. Enhanced concentrations of OH result from the photolysis of HONO that is formed in the early stages of the exhaust from emitted OH and NO. Reactive hydrogen emissions (the sum of OH and HONO) are 5% of the  $NO_x$  emissions from both aircraft, indicating that the factors that control OH and  $NO_x$  emissions from each engine are similar. Reactions of

OH with  $\text{NO}_x$  control the lifetime of HONO and, hence, oxidation by OH in the plume. Gas-phase reactions with OH oxidize only a small fraction of  $\text{NO}_x$  (5%) and  $\text{SO}_2$  (2%) in the plume, indicating that oxidation by OH is not responsible for generating the large number of particles observed in the exhaust wake of the Concorde.

The second objective of the research was to refine the water vapor observations to provide accurate, rapid time-response observations from the ER-2, to explore the behavior of water vapor in the upper troposphere and lower stratosphere. We obtained measurements of water vapor taken using a fast-response Lyman-alpha hygrometer mounted on the NASA ER-2 for the Central Equatorial Pacific Experiment (CEPEX). The flights originated from Fiji (17°S, 178°E) and covered a range of potential temperatures up to 470 K. Concurrent ozone measurements and a 1-D model are used to convert potential temperature to effective age of the air in the stratosphere. This analysis provides insight into measured water vapor profiles in the lower tropical stratosphere, taken during different seasons on previous aircraft campaigns. It yields a picture of a seasonal cycle consistent with the variation of the average tropical tropopause temperature and an annually averaged mixing ratio of water in air entering the tropical stratosphere of about 4.45 ppmv.

In the last category of research objectives, we review progress in the development of the  $\text{ClONO}_2$  instrument that is destined for the left wing pod of the NASA ER-2. Key developments in that work occurred in calendar year 1995. The entire instrument was prototyped in the laboratory. This includes the solid state laser system for  $\text{NO}_2$  detection, the plasma discharge system for ClO and BrO detection, two solid state dissociation elements used to thermally decompose  $\text{ClONO}_2$ , and the electronics to both control all subsystems of the experiment and to obtain data from both analog and digital inputs. Calibration of both  $\text{NO}_2$  and ClO axes were performed, demonstrating that one  $\text{NO}_2$  molecule is produced for each  $\text{ClONO}_2$  dissociation event. The yield of ClO from the dissociation is 25% less than that for  $\text{NO}_2$ —an issue isolated to the high temperature calibration of the ClO detection axes.

The prototype laboratory instrument has been designed into a configuration compatible with the weight and structure of the ER-2 wing pod and all components are now under fabrication, as are the flight electronics. The instrument, supported in part by ERAST funds, is scheduled for test flights in June 1996.